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# PATENT SPECIFICATION

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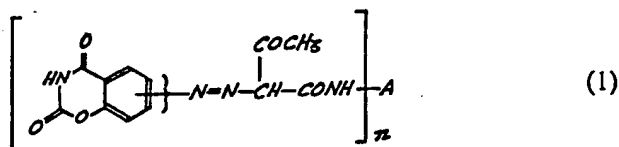
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## (54) AZO PIGMENTS AND PROCESS FOR THEIR PREPARATION

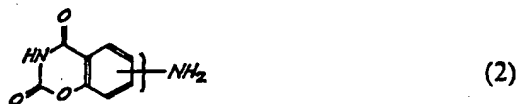
(71) We, HOECHST AKTIENGESELLSCHAFT (formerly known as Farbwerke Hoechst Aktiengesellschaft, vormals Meister Lucius & Brüning), a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt (Main) 80, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention provides azo pigments of the general formula (1)

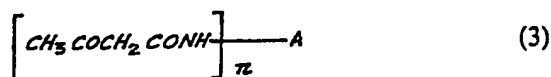


in which  $n$  is 1 or 2 and A represents a radical of the benzene, naphthalene or benzimidazolone series when  $n$  is 1 or a radical of the benzene or diphenyl series when  $n$  is 2, which radical represented by A may be substituted.

The present invention also provides a process for preparing the above-mentioned pigments which comprises diazotizing an amino-benzoxazine-dione of the general formula (2)



and coupling the product with a coupling component of the general formula (3)



in which  $n$  and A are defined as above.

Of the amino-benzoxazine-diones used, the 6-amino-1,3-benzoxazine-2,4-dione is described in French Patent Specification No. 1,368,739. The 7-amino-1,3-benzoxazine-2,4-dione, which was unknown, can be prepared according to known methods, for example by catalytic hydrogenation of the corresponding nitro compound (cf. C. Wagner and D. Singer, Pharm. Zentralhalle 103, 791 (1964).

The compounds used as coupling components of the general formula (3) are generally described in the literature, and can be prepared according to known methods, for example by reacting an aromatic mono- or diamine with diketene or acetoacetic acid methyl ester.

Preferred coupling components are N-acetoacetylaminonaphthalenes; N-acetoacetylanilines in which the phenyl nucleus may be substituted by 1 to 3

carbon atoms, preferably methyl and ethyl groups, alkoxy groups having 1 to 4 carbon atoms, preferably methoxy and ethoxy groups, and acetyl and acetylamino groups; N-acetoacetyl-amino-benzimidazolones which may be substituted by a chlorine or bromine atom in the 6- or 7-position; and bis-acetoacetyl-amino-benzenes and -diphenyls which may be substituted in the phenyl ring(s) by one or two substituents selected from chlorine and bromine atoms and methyl and methoxy groups. Of the N-acetoacetyl-anilines which are substituted in the phenyl nucleus by one or more acetyl and/or acetylamino groups, those that do not contain more than one substituent selected from the acetyl and acetylamino groups are preferred.

Coupling components of this type are:

5	N-acetoacetyl-aniline	
	1-acetoacetyl-amino-naphthalene	
	N-acetoacetyl-2-chloro-aniline	
15	N-acetoacetyl-4-chloro-aniline	15
	N-acetoacetyl-2,4-dichloro-aniline	
	2-acetoacetyl-amino-anisole	
	4-acetoacetyl-amino-anisole	
	4-acetoacetyl-amino-phenetole	
20	N-acetoacetyl-2,5-dimethoxy-aniline	20
	N-acetoacetyl-2,4-dimethoxy-aniline	
	N-acetoacetyl-4-chloro-2,5-dimethoxy-aniline	
	N-acetoacetyl-5-chloro-2,4-dimethoxy-aniline	
	2-acetoacetyl-amino-toluene	
25	4-acetoacetyl-amino-toluene	25
	4-acetoacetyl-amino-1,3-xylene	
	4-acetoacetyl-amino-acetanilide	
	2-acetoacetyl-amino-5-chloro-toluene	
	2-acetoacetyl-amino-5-acetylanisole	
30	2-acetoacetyl-amino-5-acetylamino-4-chloro-toluene	30
	N-acetoacetyl-amino-4-bromo-aniline	
	2-acetoacetyl-amino-3-chloro-toluene	
	2-acetoacetyl-amino-4-methyl-anisole	
	N-acetoacetyl-2,5-dimethoxy-4-bromo-aniline	
35	N-acetoacetyl-2,5-diethoxy-4-chloro-aniline	35
	N-acetoacetyl-4,5-dimethoxy-2-chloro-aniline	
	N-acetoacetyl-2,5-dichloro-aniline	
	N-acetoacetyl-2,4-diethoxy-aniline	
	N-acetoacetyl-4-ethyl-aniline	
40	N-acetoacetyl-2,4,6-trimethyl-aniline	40
	3-acetoacetyl-4-bromo-6-methyl-anisole	
	2-acetoacetyl-amino-5-bromo-anisole	
	2-acetoacetyl-amino-4-methyl-anisole	
	2-acetoacetyl-amino-5-methyl-6-bromo-phenetole	
45	5-acetoacetyl-amino-benzimidazolone	45
	5-acetoacetyl-amino-6-chloro-benzimidazolone	
	5-acetoacetyl-amino-7-chloro-benzimidazolone	
	1,4-bis-acetoacetyl-amino-2-bromo-benzene	
	1,4-bis-acetoacetyl-amino-benzene	
50	1,4-bis-acetoacetyl-amino-2-chloro-benzene	50
	1,4-bis-acetoacetyl-amino-2,5-dichloro-benzene	
	2,5-bis-acetoacetyl-amino-toluene	
	2,5-bis-acetoacetyl-amino-1,4-xylene	
	2,5-bis-acetoacetyl-amino-anisole	
55	1,4-bis-acetoacetyl-amino-2,5-dimethoxy-benzene	55
	2,5-bis-acetoacetyl-amino-4-methoxy-toluene	
	N,N'-bis-acetoacetyl-3,3'-dichloro-benzidine	
	N,N'-bis-acetoacetyl-2,2'-dichloro-benzidine	
	N,N'-bis-acetoacetyl-3,3'-dimethoxy-benzidine	
60	N,N'-bis-acetoacetyl-3,3'-dimethyl-benzidine	60

The azo pigments of the invention may be prepared according to known methods, for example, by coupling the diazotized aminobenzoxazinediones with the coupling components in an aqueous medium, preferably in the presence of a

organic solvent. The coupling reaction can also be performed in an organic solvent.

The diazonium salts of the amino-benzoxazinediones have a poor solubility in water. Therefore, the diazotization can also be carried out, advantageously, in a suitable organic medium, for example in glacial acetic acid, alcohols, formamide, dimethyl formamide or dimethyl sulfoxide. The solution of the diazonium salt so obtained can then be combined with the coupling component.

To obtain the full tinctorial strength and an especially favourable crystal structure, it is often advantageous to after-treat the azo pigment obtained, for example by heating the moist or dried and ground pigment in pyridine, dimethylformamide or other organic solvent, such as dimethyl sulfoxide, alcohol, chlorobenzene, dichlorobenzene, glacial acetic acid, quinoline, glycol or nitrobenzene, under reflux conditions or at an elevated temperature under pressure for a certain period of time. In some cases, an especially favourable crystal structure can also be obtained by heating with water to the boil or to an elevated temperature under pressure, optionally with the addition of one or more dispersion agents and, optionally, one or more organic solvents, for example those of the type mentioned above.

The azo pigments of the invention are water-insoluble. They are suitable for the manufacture of colored lacquers, lacquer forming agents, solutions and products made of acetyl cellulose, natural resins or synthetic resins, such as polymerization or condensation resins, for example amino- or phenoplasts, as well as those made of polystyrene, polyolefins, for example polyethylene, polyacrylo compounds, polyvinyl compounds, for example polyvinyl chloride or polyvinyl acetate, polyesters, rubber, casein or silicone resins.

The pigments of the invention are also suitable for pigment printing on substrates, especially on textile fibrous materials or other flat-surface structures, for example paper.

The pigments can also be used for other application purposes, for example in a finely dispersed form for dyeing viscose rayon, cellulose ethers or esters, polyamides, polyurethanes, polyglycol terephthalates or polyacrylonitrile in the spinning mass, or for dyeing paper. The pigments of the invention show good fastness to light, to weather and to migration in the media mentioned. Furthermore, they are stable towards heat, have a good tinctorial strength and show pure shades in many cases. They are stable towards the action of chemicals, in particular solvents, dilute acids and alkalis.

The following Examples illustrate the invention.

#### EXAMPLE 1.

17.8 g (0.1 mol) of 7-amino-1,3-benzoxazine-2,4-dione, 60 ml of glacial acetic acid and 27.8 ml of 31% hydrochloric acid were stirred for 1 hour and diazotized at 0°C with 20 ml of 5 N sodium nitrite solution

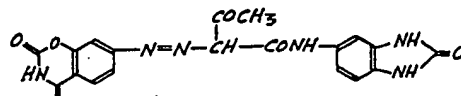
Stirring was continued for 30 minutes, the solution was diluted with ice water, again stirred for another 90 minutes and clarified.

24 g (0.103 mol) of 5-acetoacetyl-amino-benzimidazolone were dissolved in 121 ml of 2 N sodium hydroxide solution and 200 ml of water and the solution was clarified. 25.2 ml of glacial acetic acid, 50.4 ml of 2 N sodium hydroxide solution and 1 g of a mixture of the sodium salt of sinarolsulfamido-acetic acid and sinarol were placed in the coupling vessel. The temperature was adjusted to 10°C by adding ice and the solution of the coupling component was added dropwise.

Thereafter, the diazonium salt solution was slowly introduced.

The coupling being completed, a temperature of 90°C was reached by introducing steam and that temperature was maintained for 20 minutes, the pigment was suction-filtered, washed with water and dried at 65°C. The dried pigment was ground and heated to 100°C for 30 minutes with 800 ml of dimethyl formamide and 200 ml of water, whereupon the pigment turned from orange red to yellow, was suction-filtered at 60°C, washed, dried and ground.

The pigment obtained had the formula



It showed an excellent fastness to solvents and yielded, upon being worked into polyvinyl chloride, a lacquer, a printing paste or a spinning mass, pure.

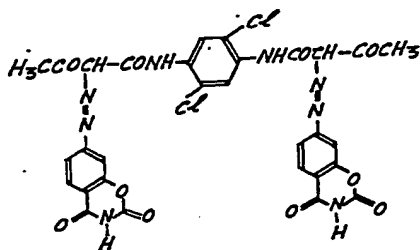
When, instead of 5-acetoacetyl-amino-benzimidazolone in the above process, the equivalent amount of 5-acetoacetyl-amino-7-chloro-benzimidazolone was used, a yellow pigment was obtained, which also yielded similar good fastness properties when worked, for example, into polyvinyl chloride.

#### EXAMPLE 2.

8.9 g of 7-amino-1,3-benzoxazine-2,4-dione were diazotized as described in Example 1.

8.7 g (0.252 mol) of 1,4-bis-acetoacetyl-amino-2,5-dichlorobenzene were dissolved in 200 ml of water and 17 ml of 33% sodium hydroxide solution, diluted with 300 ml of water and 1000 ml of isopropanol, whereafter 15 ml of glacial acetic acid were added. Then, the clarified diazonium salt solution was slowly introduced at 20°C to the coupling component, the solution was stirred for another hour and heated under reflux for 1 hour. The pigment was suction-filtered, washed with water, dried and ground, and then heated for 2 hours with 350 parts by volume of dimethyl formamide to 100°C. It was suction-filtered again, washed with methanol and water, dried and ground.

The pigment obtained had the formula



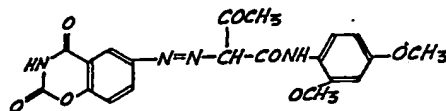
Upon being worked into polyvinyl chloride, a lacquer, a printing paste or a spinning mass, it yielded greenish yellow dyeings having a very good stability towards heat and very good fastness to light and migration.

#### EXAMPLE 3.

8.9 g (0.05 mol) of 6-amino-1,3-benzoxazine-2,4-dione, 40 ml of water and 40 ml of 5 N hydrochloric acid were stirred overnight and diazotized at a 0°C with 10 ml of 5 N sodium nitrite, diluted with water to 200 ml and clarified. 11.9 g (0.05 mol) of N-acetoacetyl-2,4-dimethoxyaniline were dissolved in 200 ml of water and 7.5 ml of 33% sodium hydroxide solution, clarified and precipitated in the presence of 2.75 g of rosin soap (of 50% strength) at 10°C with 5.1 ml of glacial acetic acid.

The diazonium salt solution was slowly added dropwise to that suspension, the pH being maintained at 4.5—5 by simultaneously introducing dilute sodium hydroxide solution. After coupling was completed, the reaction mixture was heated to 90°C for 30 minutes, the pigment was suction-filtered hot and washed with water. The moist press-cake was boiled with glacial acetic acid for 1.5 hours, suction-filtered, washed with water, dried and ground. The color strength could be improved by thermal after-treatment in 25% aqueous dimethyl formamide.

The pigment obtained had the formula



Upon being worked into polyvinyl chloride, a lacquer, a printing paste or a spinning mass, it yielded pure, yellow dyeings having good fastness to light and migration.

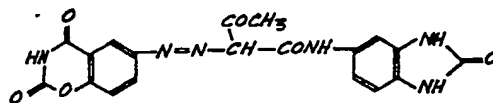
When, instead of N-acetoacetyl-2,4-dimethoxyaniline as in the above process the equivalent amount of 2-acetoacetyl-5-chloro-anisole was used, a greenish yellow pigment was obtained having similar good properties.

#### EXAMPLE 4.

8.9 g of 6-amino-1,3-benzoxazine-2,4-dione were diazotized as described in Example 1. 12.2 g (0.0525 mol) of 5-acetoacetyl-amino-benzimidazolone were

dissolved in 17 ml of 33% sodium hydroxide solution and 500 ml of isopropanol and clarified. The solution was adjusted to pH 5.5 with about 13 ml of glacial acetic acid, the diazonium salt solution was slowly introduced and heated in a heating bath to 70°—80°C for 30 minutes after coupling had been completed. The pigment was suction-filtered, washed with water, dried and ground. After a short thermal after-treatment at 100°C with a mixture of dimethylformamide, glacial acetic acid and water (2/1/1) it was again suction-filtered, washed with water and dried.

The pigment obtained had the formula

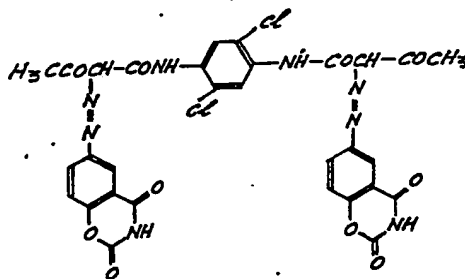


Upon being worked into polyvinyl chloride, a lacquer, a printing paste or a spinning mass, it yielded greenish yellow dyeings having excellent fastness to light and migration.

#### EXAMPLE 5.

8.9 g of 6-amino-1,3-benzoxazine-2,4-dione were diazotized as described in Example 3. 8.7 g (0.0252 mol) of 1,4-bisacetoacetylamino-2,5-dichlorobenzene were dissolved in 200 ml of water and 17 ml of 33% sodium hydroxide solution, clarified, diluted with 280 ml of water and 500 ml of isopropanol and partially precipitated with 15 ml of glacial acetic acid. The diazonium salt solution was slowly added dropwise, the mixture was stirred for 2 hours, boiled under reflux for 1 hour and suction-filtered while hot. The press-cake was washed with water, pasted again with 500 ml of glacial acetic acid and boiled under reflux for 1 hour. It was suction-filtered, washed with water, dried and ground. By treating the pigment with dimethyl formamide for 1 hour at 120°C the covering power could be further improved.

The pigment obtained had the formula



Upon being worked into polyvinyl chloride, a lacquer, a printing paste or a spinning mass, it yielded greenish yellow dyeings of very good fastness to light and migration.

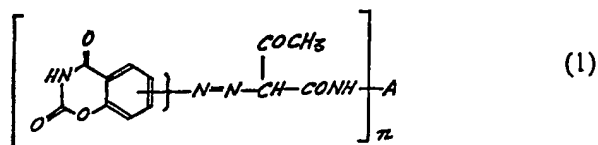
The following Table contains a list of further components which can be used in accordance with the invention, as well as the shades of the graphic prints using the pigments prepared therefrom.

Diazo component	Coupling component	Shade
6-amino-1,3-benzoxazine-2,4-dione	N-acetoacetyl aniline	yellow
"	1-acetoacetyl-amino-naphthalene	yellow
"	N-acetoacetyl-2-chloro-aniline	greenish-yellow
"	N-acetoacetyl-4-chloro-aniline	"
"	N-acetoacetyl-2,4-dichloro-aniline	"
"	2-acetoacetyl-amino-anisole	yellow
"	4-acetoacetyl-amino-anisole	yellow
"	2-acetoacetyl-amino-toluene	yellow
"	4-acetoacetyl-amino-toluene	"
"	4-acetoacetyl-amino-1,3-xylene	"
"	N-acetoacetyl-4-chloro-2,5-dimethoxy-aniline	"
"	2-acetoacetyl-amino-5-chloro-toluene	"
"	2-acetoacetyl-amino-5-acetyl-amino-4-chloro-toluene	"
"	5-acetoacetyl-amino-7-chloro-benzimidazolone	"
"	1,4-bis-acetoacetyl-amino-benzene	"
"	1,4-bis-acetoacetyl-amino-2-chloro-benzene	"
"	2,5-bis-acetoacetyl-amino-toluene	"
"	2,5-bis-acetoacetyl-amino-1,4-xylene	reddish yellow
"	2,5-bis-acetoacetyl-amino-anisole	"
"	2,5-bis-acetoacetyl-amino-4-methoxy-toluene	reddish

Diazo component	Coupling component	Shade
6-amino-1,3-benzoxazine-2,4-dione	N,N'-bis-acetoacetyl-3,3'-dimethyl-benzidine	yellow
"	N,N'-bis-acetoacetyl-2,2'-dichloro-benzidine	yellow
"	N,N'-bis-acetoacetyl-3,3'-dimethoxy-benzidine	yellow
7-amino-1,3-benzoxazine-2,4-dione	2-acetoacetyl-amino-anisole	"
"	4-acetoacetyl-amino-anisole	"
"	2-acetoacetyl-amino-toluene	"
"	4-acetoacetyl-amino-toluene	"
"	N-acetoacetyl-2,4-dimethoxy-aniline	"
"	N-acetoacetyl-2,5-dimethoxy-aniline	"
"	2-acetoacetyl-5-chloro-anisole	greenish-yellow
"	N-acetoacetyl-4-chloro-2,5-dimethoxy-aniline	yellow
"	1,4-bis-acetoacetyl-amino-benzene	yellow
"	1,4-bis-acetoacetyl-amino-2-chlorobenzene	yellow
"	1,4-bis-acetoacetyl-amino-anisole	reddish yellow
"	1,4-bis-acetoacetyl-amino-anisole-2,5-dimethoxy-benzene	"
"	2,5-bis-acetoacetyl-amino-1,4-xylene	"

WHAT WE CLAIM IS:—

1. An azo pigment of the general formula (1)

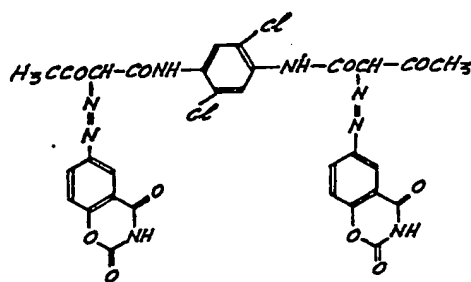


2. A pigment as claimed in claim 1, wherein  $n$  is 1 and A represents a naphthyl radical, an unsubstituted phenyl radical, a phenyl radical substituted by 1 to 3 substituents selected from chlorine and bromine atoms, alkyl groups having 1 to 4 carbon atoms, alkoxy groups having 1 to 4 carbon atoms and acetyl and acetylamino groups, an unsubstituted benzimidazolone radical or a benzimidazolone radical substituted in the 6- or 7-position by a chlorine or bromine atom.

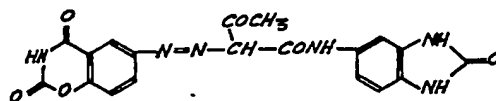
3. A pigment as claimed in claim 2, wherein a substituted phenyl radical represented by A does not contain more than one substituent selected from the acetyl and acetylamino groups.

4. A pigment as claimed in claim 1, wherein  $n$  is 2 and A represents an unsubstituted phenylene or biphenylene radical or a phenylene or biphenylene radical substituted by 1 or 2 substituents selected from chlorine and bromine atoms and methyl and methoxy groups.

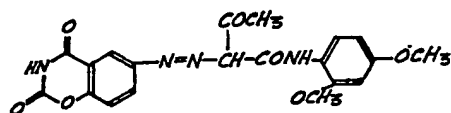
5. A pigment as claimed in claim 1 of the formula



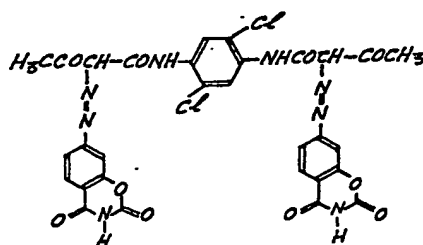
6. A pigment as claimed in claim 1 of the formula



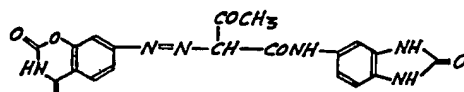
7. A pigment as claimed in claim 1 of the formula



8. A pigment as claimed in claim 1 of the formula



9. A pigment as claimed in claim 1 of the formula



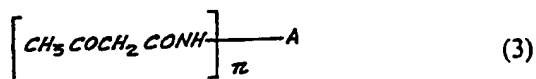
10. A pigment as claimed in claim 1 and described herein.



11. A process for preparing a pigment of the general formula (1) given in claim 1, which comprises diazotizing an amino-benzoxazine-dione of the general formula (2)



5 and coupling the product with a coupling component of the general formula (3) 5



in which n and A are as defined in claim 1.

12. A process as claimed in claim 11, wherein the coupling component is any one of those specifically mentioned herein.

10 13. A process as claimed in claim 11 or claim 12, wherein the diazotization reaction is carried out in an organic solvent. 10

14. A process as claimed in claim 13, wherein the organic solvent is glacial acetic acid, an alcohol, formamide, dimethyl formamide or dimethylsulphoxide.

15 15. A process as claimed in any one of claims 11 to 14, wherein the coupling reaction is carried out in an aqueous medium. 15

16. A process as claimed in claim 15, wherein the coupling reaction is carried out in the presence of a non-ionic, anion active or cation active dispersing agent or an organic solvent.

20 17. A process as claimed in any one of claims 11 to 16, wherein the pigment is subjected to an after-treatment at an elevated temperature in an organic solvent or water. 20

18. A process as claimed in claim 11, conducted substantially as described herein.

25 19. A process as claimed in claim 17, conducted substantially as described herein. 25

20. An azo pigment as claimed in claim 1, whenever prepared by a process as claimed in any one of claims 11 to 19.

30 21. A colouring, dyeing or printing process wherein an azo pigment as claimed in any one of claims 1 to 10 and 20 is used. 30

22. A lacquer, a lacquer forming agent, a solution or product made of acetyl cellulose, a natural or synthetic resin or polymer or paper, whenever coloured or dyed with an azo pigment as claimed in any one of claims 1 to 10 and 20.

35 23. An aminoplast, phenoplast, viscose rayon, cellulose ether or ester, polystyrene, polyolefin, polyacrylo compound, polyvinyl compound, polyester, polyamide, polyurethane, rubber, casein or silicone resin, whenever coloured or dyed with an azo pigment as claimed in any one of claims 1 to 10 and 20. 35

24. A textile material or paper, whenever printed with a pigment as claimed in any one of claims 1 to 10 and 20.

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